

REMARKS

Claims 1-3, 5, 9-11, and 21 are pending in this application. Claim 3 was cancelled. Claims 1 and 5 were amended and new claims 23-29 were added to more distinctly claim the invention. Support for the new and amended claims can be found in the specification. No new matter has been added.

Attached is a marked-up version of the changes made to the claims by the current amendment. The attached page is captioned "VERSION WITH MARKINGS TO SHOW CHANGES MADE."

The Examiner objected to certain references in the information disclosure statement. A copy of the Japanese Patent 75229 and U.S. Application Serial Number 09/268,203 were not included. To overcome such objections, Applicants submit U.S. Patent No. 5,089,441 that is related to the Japanese patent as evidenced by the attached search results for Dialog. Applicants also include a copy of U.S. Serial Number. 09/268,203, commonly assigned.

Claim 1 is objected to. The term "undesirable influence" does not include a positive limitation. Accordingly, Applicants have provided such limitation in claim 1, as shown above, as discussed with the Examiner. Applicants have also changed the "containing" language in claim 1. Accordingly, claim 1 should be free from any objections.

Claims 1-3, 5, 9-11, and 21 were rejected under 35 U.S.C. §112, first paragraph. Applicants have discussed such rejection with Examiner Ahmed. Claim 1 has been amended to eliminate the recitation of "atoms," which should render the rejection moot. The Examiner also rejected claims 1-3, 5, 9-11, and 21 under 35 U.S.C. §112, second paragraph. Accordingly, claim 1 has been amended, which should render the objection moot.

New claims 23 through 29 were added. No new matter has been introduced thereby. Applicants respectfully request for such claims to be added for

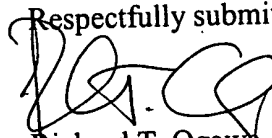
SHUZO FUJIMURA et al.
Application No.: 09/328,939
Page 5

examination and allowance. Such claims were derived from claims 1-3, 9, 9-11, and 21, which have been pending.

CONCLUSION

In view of the foregoing, Applicants believe all claims now pending in this Application are in condition for allowance and an action to that end is urged. If the Examiner believes a telephone conference would aid in the prosecution of this case in any way, please call the undersigned at 650-326-2400.

Respectfully submitted,



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VERSION WITH MARKINGS TO SHOW CHANGES MADE

1. (Amended) A method of surface treatment in a substantially downstream position of a plasma source to substantially **[prevent]** be free from an undesirable influence of a reactive species from the plasma source, where an object to be processed is downstream from the plasma source, the method comprising generating a plasma discharge including a gas-C, the gas-C comprising a Gas-A molecule **[containing]** including essentially hydrogen as an element and a Gas-B **[containing]** including essentially a **[halogen and/or]** a halide; wherein said plasma discharge is substantially free from an oxygen bearing species; and wherein the Gas B is selected from **[chlorine,]** hydrogen chloride[, **bromine,**] or hydrogen bromide; wherein Gas C comprises a flow rate defined as a ratio of an amount of hydrogen **[atom]** in Gas-B to that in Gas-A is larger than 1/480.

2. The method of claim 1 further comprising injecting a Gas-D in the downstream of the plasma of Gas-C to treat the object comprising a surface in a downstream position of the Gas-D injection.

3. (Canceled)

5. (Amended) The method of claim 1 **[3]**, wherein Gas-B does not contain an oxygen atom.

9. The method of claim 2, wherein gas containing silicon as its element is used as Gas-D.

10. The method of claim 2, wherein gas containing carbon as its element is used as Gas-D.

11. The method of claim 2, wherein gas containing fluorine as its element is used as Gas-D.

21. The method of claim 1 wherein the method is provided to substantially prevent physical damage caused by a high energy particle.

23. (New) A method of surface treatment in a substantially downstream position of a plasma source, where an object to be processed is downstream from the plasma source, the method comprising generating a plasma discharge including a gas-C, the gas-C comprising a Gas-A molecule including essentially hydrogen as an element and a Gas-B including essentially a halogen and a hydrogen bearing species; wherein said plasma discharge is substantially free from an oxygen bearing species; and wherein the Gas B is selected from at least a chlorine, bromine, iodine, or fluorine; wherein Gas C comprises a flow rate defined as a ratio of an amount of hydrogen in Gas-B to that in Gas-A is larger than 1/480.

24. (New) The method of claim 23 further comprising injecting a Gas-D in the downstream of the plasma of Gas-C to treat the object comprising a surface in a downstream position of the Gas-D injection.

25. The method of claim 23 wherein Gas-B does not contain an oxygen atom.

26. The method of claim 23 wherein gas containing silicon as its element is used as Gas-D.

27. The method of claim 23 wherein gas containing carbon as its element is used as Gas-D.

28. The method of claim 23 wherein gas containing fluorine as its element is used as Gas-D.

29. The method of claim 23 wherein the method is provided to substantially prevent physical damage caused by a high energy particle.

Dialog Search for: H7-75229
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1/9/1

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PATENT FAMILY:

GERMANY (DE)

Patent (No,Kind,Date): DE 69130909 C0 19990401

PLASMABEHANDLUNGSVERFAHREN EINES RESISTS UNTER VERWENDUNG VON
WASSERSTOFFGAS (German)

Patent Assignee: FUJITSU LTD (JP)

Author (Inventor): FUJIMURA SHUZO (JP); TAKEUCHI TATSUYA (JP);
NAKANO YOSHIMASA (JP); MIYANAGA TAKESHI (JP); MATOBA YUUJI (JP)

Priority (No,Kind,Date): JP 90168905 A 19900626

Applic (No,Kind,Date): DE 69130909 A 19910626

IPC: * H01L-021/3105; H01L-021/312; H01L-021/306; C23C-016/02

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Language of Document: German

Patent (No,Kind,Date): DE 69130909 T2 19990624

PLASMABEHANDLUNGSVERFAHREN EINES RESISTS UNTER VERWENDUNG VON
WASSERSTOFFGAS (German)

Patent Assignee: FUJITSU LTD (JP)

Author (Inventor): FUJIMURA SHUZO (JP); TAKEUCHI TATSUYA (JP);
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Priority (No,Kind,Date): JP 90168905 A 19900626

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IPC: * H01L-021/3105; H01L-021/312; H01L-021/306; C23C-016/02

CA Abstract No: * 116(16)164612R

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GERMANY (DE)

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EUROPEAN PATENT OFFICE (EP)

Patent (No,Kind,Date): EP 463870 A1 19920102

PLASMA TREATING METHOD USING HYDROGEN GAS (English; French; German)

Patent Assignee: FUJITSU LTD (JP)

Author (Inventor): FUJIMURA SHUZO (JP); TAKEUCHI TATSUYA (JP);
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 Patent (No,Kind,Date): EP 463870 B1 19990224
 METHOD OF PLASMA TREATING A RESIST USING HYDROGEN GAS (English; French;
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 Patent Assignee: FUJITSU LTD (JP)
 Author (Inventor): FUJIMURA SHUZO (JP); TAKEUCHI TATSUYA (JP);
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EP 463870	P	19941012	EP 17Q	FIRST EXAMINATION REPORT (ERSTER PRUEFUNGSBESCHEID)	940829
EP 463870	P	19990224	EP AK	DESIGNATED CONTRACTING STATES MENTIONED IN A PATENT SPECIFICATION: (IN EINER PATENTSCHRIFT ANGEFUEHRTE BENANNTEN VERTRAGSSTAATEN)	DE FR GB IT
EP 463870	P	19990224	EP B1	PATENT SPECIFICATION (PATENTSCHRIFT)	
EP 463870	P	19990401	EP REF	CORRESPONDS TO: (ENTSPRICHT)	DE 69130909 P 19990401
EP 463870	P	19990511	EP ITF	IT: TRANSLATION FOR A EP PATENT FILED (IT: DEPOSITO TRADUZIONE DI BREVETTO EUROPEO)	STUDIO JAUMANN P. & C. S.N.C.
EP 463870	P	19990604	EP ET	FR: TRANSLATION FILED (FR: TRADUCTION A ETE REMISE)	
EP 463870	P	20000216	EP 26N	NO OPPOSITION FILED (KEIN EINSPRUCH EINGELEGT)	
EP 463870	P	20020101	GB IF02/REG	EUROPEAN PATENT IN FORCE AS OF 2002-01-01	

JAPAN (JP)

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PLASMA PROCESSING METHOD (English)

Patent Assignee: FUJITSU LTD

Author (Inventor): FUJIMURA SHUZO; TAKEUCHI TATSUYA; MIYANAGA TAKESHI;
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Applic (No,Kind,Date): JP 91153493 A 19910625

IPC: * H01L-021/302; B01J-019/08; C23F-004/00; H01L-021/205;
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Language of Document: Japanese

Patent (No,Kind,Date): JP 95075229 B4 19950809

Priority (No,Kind,Date): JP 91153493 A 19910625; JP 90168905 A
19900626

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CA Abstract No: * 116(16)164612R

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Language of Document: Japanese

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Patent (No,Kind,Date): KR 9405287 B1 19940615

PLASMA TREATING METHOD USING HYDROGEN GAS (English)

Patent Assignee: FUJITSU LTD (JP)

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Priority (No,Kind,Date): JP 90168905 A 19900626

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UNITED STATES OF AMERICA (US)

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PLASMA TREATING METHOD USING HYDROGEN GAS (English)

Patent Assignee: FUJITSU LTD (JP)

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Priority (No,Kind,Date): US 272519 A 19940711; JP 90168905 A
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US 5403436	P	19910625	US AA	PRIORITY
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US 5403436	P	19930630	US AA	PRIORITY
			US 93906 B1	19930630
US 5403436	P	19940711	US AE	APPLICATION DATA (PATENT)

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PATENT APPLICATION

PLASMA SURFACE TREATMENT METHOD AND RESULTING DEVICE

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PLASMA SURFACE TREATMENT METHOD AND RESULTING DEVICE

CROSS-REFERENCES TO RELATED APPLICATIONS

5 This application claims priority to U.S. Serial No. 60/078,321 filed March 17, 1998, commonly assigned and hereby incorporated by reference for all purposes.

BACKGROUND OF THE INVENTION

10 The present invention relates to objects and their manufacture. More particularly, the invention is illustrated in an example using a novel combination of gases and a downstream plasma surface for selectively removing photoresist materials for substrates used in semiconductor integrated circuits. Merely by way of example, the invention can be applied in the manufacture of other substrates such as flat panel displays, micro electrical mechanical machines ("MEMS"), sensors, optical devices, and others.

15 In the manufacture of objects such as integrated circuits, processing safety and reliability have been quite important. Fabrication of integrated circuits generally require numerous processing steps such as etching, deposition, photolithography and others. In the photolithography process, for example, a photoresist film of material is often used to form patterns on thin slices of silicon or films that are deposited on such silicon. After patterning, however, it is necessary to remove the photoresist film from the silicon using a hydrogen bearing compound. Additionally, hydrogen bearing compounds are used in plasma treatment of silicon surfaces. In some cases, hydrogen is used to terminate ends of silicon bonds.

20 Hydrogen is also used to remove oxides. Numerous studies have been made in using a hydrogen bearing compound, and in particular a low temperature process using a reductive reaction from atomic hydrogen produced by a hydrogen gas molecule gas plasma. For example, an object such as a wafer or hard disk has a surface, which is to be processed at a certain area or reactor exposed to high energy species such as ions

25 even in the plasma downstream system. This way of processing occurs because lifetime of atomic hydrogen generated in the plasma is often short and can easily recombine into hydrogen molecules outside of the plasma discharge area. Thus, the conventional

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process often cannot avoid damage caused by high-energy species such as ions and electrons, decreasing the controllability of processing.

Numerous techniques using hydrogen for processing devices have been reported. As merely an example, a conventional process for ashing organic material, which is carbonized by ion implantation, using atomic hydrogen in a downstream plasma of hydrogen diluted by nitrogen or argon, has been reported by in a paper by S. Fujimura, H. Yano, J. Konno, T. Takada, and K. Inayoshi: Study on ashing process for removal of ion implanted resist layer, Process Symposium, Dry Process, Procedure Vol. 88-7, Honolulu, Hawaii, May, 1987 (The Electrochemical Society Inc. Pennington, 1988) pp. 126-133, which is incorporated herein by reference herein. It also has been reported that a high concentration atomic hydrogen is obtained in plasma downstream by the use of mixture of hydrogen and water vapor as the source gas for the plasma in J. Kikuchi, S. Fujimura, M. Suzuki, and H. Yano, Effects of H₂O on atomic hydrogen generation in hydrogen plasma, Jpn. J. Appl. Phys., 32, pp. 3120-3124 (1993) ("Kikuchi, et al."), which is incorporated by reference herein. Kikuchi et al. proposes a method to make an environment of a high concentration of atomic hydrogen at a downstream region where the influence of substantially all high energy species such as ions, electrons, and photons generated by plasma discharge can be substantially ignored.

Moreover, it was discovered that silicon native oxide could be eliminated at low temperature using NF₃ injected downstream of a H₂+H₂O plasma. This has been reported by J. Kikuchi, M. Iga, H. Ogawa, S. Fujimura, and H. Yano, Native oxide removal on Si surface by NF₃-added hydrogen and water vapor plasma downstream treatment, Jpn. J. Appl. Phys., 33, 2207-2211 (1994). This silicon native oxide removal process with NF₃-added hydrogen and water vapor plasma downstream treatment achieved a removal of silicon native oxide at nearly room temperature in vacuum environment and formation of hydrogen terminated silicon surface. Thus, the reported process can replace the conventional high temperature hydrogen gas pre-treatment of silicon epitaxy. J. Kikuchi, M. Nagasaka, S. Fujimura, H. Yano, and Y. Horiike, "Cleaning of Silicon Surface by NF₃-Added Hydrogen and Water-Vapor Plasma Downstream Treatment," Jpn. J. Appl. Phys., 35, 1022-1026 (1996).

Additionally, it was suggested to use this method for the several applications of a silicon

based semiconductor-manufacturing process such as cleaning of a contact hole of ULSI devices, J. Kikuchi, M. Suzuki, K. Nagasaka, and S. Fujimura. The silicon native oxide removal with using NF_3 -added hydrogen and water vapor plasma downstream treatment 4. Extended Abstracts (The 44th Spring Meeting, 1997); The Japan Society of Applied Physics and Related Societies, 1997, (29p-W6) in Japanese.).

The aforementioned technologies generally required introducing a high concentration of a hydrogen gas into a plasma. The high concentration of hydrogen causes an absolute risk of an explosion. Accordingly, a high-level safe system has to be prepared for practical use of this technology. For example, restrictions of the use of rotary vacuum pump with conventional vacuum pump oil should be prepared. A requirement of a vacuum load lock system in order to prevent the leaking of hydrogen from reaction reactor also need be prepared. A further requirement would include a high volume dilution inert gas system at exhaust pump gas in order to reduce the concentration of hydrogen lower than its explosion limit. Moreover, the system would also require a hydrogen gas leak-monitoring system, a fire extinguishing system, and an alarm system for the inside of equipment or installed room itself. These safety requirements will generally result in high costs to use this technology and it will become an obstacle to the growth of the technology in the industry.

From the above, it is seen that an improved technique of fabricating a substrate in an easy, cost effective, and efficient manner is often desirable.

SUMMARY OF THE INVENTION

According to the present invention, a technique including a method and device for the manufacture of treating objects is provided. In an exemplary embodiment, the present invention provides a novel technique for treating a surface of an object using a plasma treatment apparatus.

In a specific embodiment, the present invention provides a method for treating a surface of an object using, for example, a downstream region of a plasma source. The method includes a step of generating a plasma from a gas-C in a plasma source, where the gas-C includes a gas-A and a gas-B. Gas-A is selected from a compound comprising at least a nitrogen bearing compound or an other gas. The other gas is selected from a mixture of an element in group 18 classified in the atomic

periodic table. Gas-B includes at least a NH_3 bearing compound. The method also includes a step of injecting a gas-D downstream of the plasma source of the gas C. The method also includes a step of setting an object (having a surface) downstream of the gas-D injection and downstream of the plasma source. A step of processing the surface of the object by a mixture species generated from the gas-C in the plasma and the gas-D is included. The NH_3 bearing compound in the gas-C includes a NH_3 bearing concentration that is lower than an explosion limit of NH_3 , which is safer than conventional techniques.

In a specific embodiment, the present invention provides an apparatus for processing an object. The apparatus includes a chamber and a plasma discharge room coupled to the chamber. A susceptor holds the object, i.e., wafer, display, panel. The plasma discharge room is downstream from the chamber. The apparatus also has a first gas supply comprising a gas A coupled to the plasma discharge room, where the gas A comprises a nitrogen bearing compound. The apparatus also has a second gas supply comprising a gas B coupled to the plasma discharge room, where the gas B comprises an NH_3 bearing compound. A third gas supply with a gas D coupled between the plasma discharge room and the chamber also is included. The present apparatus does not generally require load locks or the like, which are often used with conventional hydrogen processing tools.

The present invention achieves these benefits in the context of known process technology. However, a further understanding of the nature and advantages of the present invention may be realized by reference to the latter portions of the specification and attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a simplified drawing of a system according to an embodiment of the present invention;

Fig. 2 is a simplified cross-sectional view drawing of an apparatus according to an embodiment of the present invention;

Fig. 3 shows a concentration of atomic hydrogen in a $\text{H}_2\text{O} + \text{N}_2$ gas plasma vs. H_2O ratio of total plasma gas flow according to an embodiment of the present invention;

Fig. 4 shows a simplified relation between an etching speed of silicon dioxide and an atomic hydrogen concentration in a downstream area using the system of Fig. 1;

5 Fig. 5 shows etching depth of SiO₂ as a function of gas flow ratio of water-vapor and nitrogen with water-vapor diluted with nitrogen mixed gas plasma due to 500 watt, 2.45 GHz microwave and added NF₃ into down flow section under a pressure 2.0 Torr and a processing time of 3 minute;

10 Fig. 6 shows a dependence of etching depth of SiO₂ on the mixing ratio of water vapor and nitrogen in a surface treatment using equipment shown in Fig. 2, for example; and

Fig. 7 is a simplified cross-sectional view diagram of a barrel type plasma ashing system according to an embodiment of the present invention.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

15 According to the present invention, a technique including a method and device for the manufacture of treating objects is provided. In an exemplary embodiment, the present invention provides a novel technique for treating a surface of an object using a plasma treatment apparatus.

20 In a specific embodiment, the invention relates to a surface material treatment method with use of the plasma producing atomic hydrogen, for example. The invention also relates to a surface treatment method using atomic hydrogen which is produced by a plasma. In an alternative embodiment, the present invention uses a catalytic action of nitrogen, helium, neon, argon, krypton, xenon and/or radon, as well as other elements, as a part of a plasma source gas. The invention also uses a step of
25 applying under a downstream plasma method which has features of being substantially free from physical surface damage. In some of these embodiments, the present invention also reduces or minimizes inappropriate active species for the purpose of treatment, thereby providing a more efficient and effective process. Accordingly, the present invention can provide advantages such as decreased costs and increased safety in
30 surface treatment of a downstream plasma generating atomic hydrogen, for example.

For easier reading, we have prepared the following list of items and their names, which are shown in the Figs. for referencing or cross-referencing purposes.

These names are merely shown for illustration purposes and should not limit the scope of the claims herein. One of ordinary skill in the art would recognize other variations, modifications, and alternatives.

1. #1 Gas inlet
- 5 2. Microwave guide
3. Microwave cavity
4. #2 Gas inlet
5. Chamber
6. Treatment room
- 10 7. Silicon substrate
8. Exhaust
11. Plasma discharge room
12. Gas-A supply unit
13. Gas-B supply unit
- 15 14. Fitting
15. Microwave generator
16. Wave guide
17. Microwave cavity
18. Nozzle
- 20 19. Gas-D supply unit
20. Fitting
21. O-ring
22. Treatment room
23. Treatment material
- 25 24. Treatment stage
25. SiC heater unit
26. Vacuum Exhaust port
27. Loading & Unloading port
28. Inside wall
- 30 31. Quartz reaction tube
- 32a, 32b. Electrode
33. RF generator

- 34. Wafer carrier
- 35. Wafer
- 36. Cover
- 37. Aluminum etch tunnel

5 Again, the above list of names are merely shown for illustrative purposes. These names are not intended to limit the scope of the claims herein.

Before proceeding to the details of the embodiments of the present invention, it may be helpful to fully understand some of the additional limitations with conventional processing techniques. As merely an example, in an attempt to solve some of the risks associated with the above hydrogen gas techniques, Japanese Patent
10 published under KOKAI H6-338578, which is based upon the paper above (J. Kikuchi, M. Nagasaka, S. Fujimura, H. Yano, and Y. Horiike, Cleaning of Silicon Surface by NF_3 -added Hydrogen and Water-Vapor Plasma Downstream Treatment, Jpn. J. Appl. Phys., 35, 1022-1026 (1996).), describes an alternative technique. It has been
15 suggested that the capability of removing silicon native oxide by adding NF_3 gas from the down stream region of hydrogen containing gas plasma. The definition of "gas containing hydrogen" claimed in item number 1 and 4 in this official patent report, is not clear, however. The paper indicated an achievement of the objective purpose due to the reaction of atomic hydrogen and NF_3 .

20 Taking this in a broad sense, this suggests that a silicon native oxide layer would be removed by injecting NF_3 into the downstream of any plasma, which is generated with a gas containing hydrogen atoms as its element and produces atomic hydrogen. Therefore, if the same result of surface treatment in quoted paper is achievable with using H_2O molecule plasma, which is generating atomic hydrogen,
25 issues of safety and economical requirement indicated above, is solved. Additionally, water vapor is indicated, to carry a hydrogen atom described in the above quoted paper.

Fig. 1 shows a plasma down stream process system using a quartz tube similar to the Fig. in the official patent report KOKAI H6-338578. Using this system, for example, a process for trying to etch silicon thermal oxide set at a down flow region
30 of plasma has been performed under these following conditions. (Process time 30 minute, Processing pressure 1 Torr, 30 sccm H_2O as plasma source gas, 50 watt 2.54GHz microwave as plasma generating source energy, and 5 sccm NF_3 added from

down flow region of plasma.) A decrease in the thickness of the oxide was not detected in the measurement by ellipsometry. Additionally, the silicon wafer surface with a native oxide did not turn either from hydrophilic to hydrophobic after the treatment. This meant that the native oxide was not removed. The process was tested under
5 different operation conditions with changing pressure from about 0.5 Torr to about 3.0 Torr and changing flow rate of 10 sccm H₂O and 10 sccm NF₃. The result showed, however, no evidence of silicon dioxide etching.

The native oxide was not removed even using the equipment shown in Fig. 2 and got thicker in size to apply to practical treatment, under the following
10 conditions: 100sccm H₂O, 100 sccm NF₃, 500 watt 2.54GHz microwave power, processing pressure 1 Torr; and process time 10 minutes. The result showed there is no evidence of removing native silicon dioxide.

Fig. 3 shows the dependence of a concentration of atomic hydrogen in a H₂O+N₂ gas plasma on an H₂O flow ratio to total gas flow. The concentration of
15 atomic hydrogen in the plasma was measured using a actinometry method. Concrete conditions of the actinometry of atomic hydrogen are described in J.VAC. Sci. Technol. B, 9, 357-361 (1991). The result shows that the highest concentration of atomic hydrogen was observed at 100% H₂O and the concentration of atomic hydrogen decreases with decreasing in H₂O ratio monotonously.

Above experimental results indicate that an etching reaction of silicon dioxide as described in the official patent report KOKAI H6-338578 does not occur in the system with a 100 % H₂O plasma and NF₃ injection to a downstream region, through atomic hydrogen is surely generated in the plasma. Thus, an altered process with NF₃ injection into the downstream of an water vapor plasma as the source of
20 atomic hydrogen does not etch silicon dioxide though the process satisfies the necessary and sufficient condition which is the existence of atomic hydrogen and NF₃ and is described in the official patent report KOKAI H6-338578. Therefore, this process could not achieve solving the issues of safety and economical requirement.

In order to solve the above limitations, the relationship between the etch
30 velocity of silicon dioxide and hydrogen atom concentration in downstream area was investigated with the system shown in Fig. 1.

An experiment has been done as follows.

a) Generating a plasma with H₂O and N₂ mixed gas with a total gas flow of 30sccm and 2.54GHz Microwave of 50 watts.

b) Injecting NF₃ of 5 sccm into the downstream of the plasma.

c) Estimating the concentration of atomic hydrogen at 1 Torr by a calorimetry method using a shielded thermocouple, which is covered with quartz except at the tip and inserted into the area where object would be set. The calorimetry method to measure atomic hydrogen flow is described in, for example, "Young C. Kim and Michel Boudart, Recombination of O, N, and H Atoms on Silica: Kinetics and Mechanism, Langmuir, 7, 2999-3005 (1991), and L. Robbin Martin, "Diamond film growth in a flowtube: A Temperature Dependence Study", J. Appl. Phys., 70, 5667-5674 (1991)".

d) Heating a certain place of the tube up to 500 degree Celsius between the NF₂ injection point and the point where the object would be set. (Heating increases the reaction rate between atomic hydrogen and NF₃ to increase etching velocity. As the result, error in measurement in etching depth is reduced or minimized.)

e) measuring etching depth of the samples treated under several different operation conditions.

A flow rate of each gas is shown in Fig. 4 near by measurement point. Number on the left side of ":" indicates H₂O flow rate and that on the right side of ":" indicates N₂ flow rate. A unit of gas flow is measured in sccm.

In Fig. 4, the concentration of the hydrogen atom is normalized appropriately. From Fig. 4, it is clear that silicon dioxide is not etched in the treatment in 1 Torr with H₂O of relatively high concentration in the H₂O and N₂ mixed gas (from 100% to 33%) though atomic hydrogen exists at the point where the objects have been set. Under the condition of H₂O concentrations lower than 17% (H₂O flow rate is less than 5 sccm), however, silicon dioxide etch was observed and the concentration of atomic hydrogen was also relatively higher than that under the condition with high H₂O mixing ratio.

Fig. 3 shows that the concentration of atomic hydrogen in the plasma increases with the mixing ratio of H₂O ratio in the mixed gas, thus the connection of atomic hydrogen in plasma at the H₂O mixing ratio of 17% is almost 1/20 of that at 100% H₂O.

Moreover, the concentration of atomic hydrogen in the plasma at H₂O of 17% where that in the downstream was the highest is about 1/100 of atomic hydrogen concentration in the plasma at 100% H₂O. On the other hand, the concentration of hydrogen atom in the downstream at 7% H₂O is almost 13 times as large as that at 100% H₂O. These results seem to show that nitrogen generated atomic hydrogen. The disassociation ratio of 100% H₂O gas by 2.54 GHz microwave discharge is the order of ten. See L. Brown, J.Phys. Chem., 71, 2429 (1967). Even taking into consideration of the difference in plasma conditions, a disassociation ratio of H₂O in this experiment would still be several percent. If H₂O can carry atomic hydrogen toward a down flow region without a decrease in the amount of atomic hydrogen independently of operating conditions, the concentration of atomic hydrogen in the downstream would reflect that in the plasma. Thus, the fact that the numerical ratio of atomic hydrogen concentration at the 7% H₂O to that at the 100% changes from 1/100 to 13 with shift in the measurement position from the plasma to the downstream is not convinced, even if nitrogen disassociates water vapor and increases the concentration of atomic hydrogen.

Consequently, it is a reasonable interpretation that the effect of water vapor on atomic hydrogen transportation reported in the paper written by J. Kikuchi, S. Fujimura, M. Suzuki, and H. Yano is effective in the condition with a relatively lower H₂O mixing ratio in plasma source gas and ineffective in the condition with H₂O mixing ratio close to 100%, because hydroxyl radical (OH) and atomic oxygen (O) generated in the plasma quench atomic hydrogen by recombination between them. (When the small amount of H₂O was mixed into H₂, OH or O has a higher possibility to collide with a hydrogen molecule instead of atomic hydrogen, then OH and O abstract a hydrogen atom from hydrogen molecules and generate H₂O and OH and one free atomic hydrogen is simultaneously produced. In this result to be produced is a free hydrogen atom from hydrogen molecule.) Therefore, these experiments result that the carrying mechanism of atomic hydrogen from plasma to downstream with mixing nitrogen up to be majority in a N₂+H₂O mixing gas as a plasma source is different from that described in the official patent report KOKAI H6-338578 and some species with catalysis made in the plasma from the nitrogen molecule probably caused the above phenomena that atomic concentration in the downstream at H₂O mixing of several percent was larger than that at 100% H₂O.

Experimental results in 1 Torr shown in Fig. 4 seems to also show that higher atomic hydrogen concentration induces larger velocity of silicon dioxide etching. For example, however, silicon oxide was etched by 13 Å depth during 5 minutes of treatment under the condition where the treatment pressure was 2 Torr. The flow rate of water vapor and nitrogen was 2 and 28 sccm and not etched under the condition where the treatment pressure was 1 Torr and the flow rate of water vapor and nitrogen was 10 and 20 sccm, though the concentration of atomic hydrogen in the former treatment condition was about 1/8 of that in the latter. In the process performed using a gas mixed with a small amount of water vapor and nitrogen, therefore, the velocity of silicon dioxide etching caused by NF_3 injection into the downstream is not always in proportion to the concentration of atomic hydrogen. Taking consideration into the fact that the silicon dioxide etching does not occur depending upon the operating condition in spite of existence of enough amount of atomic hydrogen, this result concludes that silicon dioxide etching in this $\text{H}_2\text{O} + \text{N}_2$ process does not mainly based on the effect of atomic hydrogen and NF_3 as shown in the official patent report KOKAI H6-338578 and is caused through some other mechanism.

In Fig. 4, the operation condition giving acceptable etching rate of silicon dioxide distributes in the area showing that the flow rate of nitrogen is far larger than that of water vapor in the mixed gas. It is known that many excited nitrogen molecules with long life-time at a meta-stable energy state of which potential energy is about 10 eV are produced in plasma. The potential energy of these nitrogen molecules is enough to disassociate H_2O and NF_3 . This suggests that the etching species might be produced by another reaction such as that between H_2O and NF_2 instead of the reaction between the hydrogen atom and NF_3 . In fact, etching did not occur when N_2 and NF_3 were injected into the downstream of a 100% H_2O plasma, then few excited nitrogen existed in the downstream. Therefore, though the accurate mechanism is not clear, it is seen that the etching using the mixed gas of nitrogen and a little water vapor is mainly caused by the catalytic effect of nitrogen through plasma not caused by the mechanism depending on the reaction between hydrogen atom and NF_3 and described in the official patent report KOKAI H6-338578.

If the catalytic effect of nitrogen at meta-stable state makes it possible to use H_2O as the source of the hydrogen atom, other inert gases having long life meta-

stable energy state, such as Helium, Neon, Argon, are also available. Actually, the silicon dioxide etching phenomena has been confirmed in the treatment that NF_3 was injected into the downstream of a plasma generated using a gas composed by 90% Argon and 10% H_2O as a plasma source gas, though its etching rate was relatively smaller than that using the mixed gas of nitrogen and a few percent of water vapor.

This effect suggests that NH_3 can be used for this process instead of H_2O . NH_3 also has risk of explosion. In this process, however, the concentration of the catalytic species can be much larger than that of process species such as water vapor. Namely, for example, nitrogen containing NH_3 whose concentration is lower than its explosion limit. Actually, as shown in Fig. 6, lower concentration of NH_3 in nitrogen brought higher etching rate. The explosion limit of NH_3 in atmosphere is based predominantly on concentration. Taking gas pressure in the vacuum pump and at the exhaust port into consideration, it is preferable to use NH_3 at lower concentration than the explosion limit at atmosphere.

Fig. 2 shows the equipment for this invention. As shown is a plasma discharge section 11 for a plasma source gas made of such as quartz or alumina. Reference numeral 12 is the Gas-A supply unit and numeral 13 is the Gas-B supply unit both of which are structured with mass flow controller, valve and filter. Mixed Gas-C, which is mixed with Gas-A provided Gas-A supply unit 12 and Gas-B provided Gas-B supply unit 13, is introduced into plasma discharge room 11 through the fitting-14. Mixed Gas-C introduced into the plasma discharge room-11 is discharged into plasma by microwave, which is supplied to microwave cavity-17 through microwave guide-16 from microwave generator-15. The nozzle 18 to add another gas is set at a suitable point in the downstream region of the plasma discharge area in the plasma discharge room 11. Gas-D is injected into plasma downstream through the fitting-20 from Gas-D supplier unit-19. Gas-D supply unit is structured with mass flow controller, valve and filter. Plasma discharge room 11 is connected with treatment room 22 with O-ring 21. The surface of object 23 which placed inside of the treatment room 22, is processed by the gas which is prepared by discharged Gas-C and injected Gas-D. The object 23 is placed on stage 24 and Si-C heating unit 25 is instrumented at upper section of stage 24 in order to heat up the object 23. The treatment room 22 has vacuum exhaust port 26 and connected to the rotary vacuum pump, which is not showed in this schematic. The

treatment room 22 also has the material transport port 27 in order to load and unload the object. Inner wall part 28 can be set inside of treatment room 22 in order to protect the wall side of the treatment room or any other reason.

5 **Examples:**

1. First Example

Fig. 5 shows the dependence of etching depth of SiO_2 on the mixing ratio of water-vapor and nitrogen in the surface treatment using the equipment shown in Fig.

2. In this treatment, NF_3 of 100 sccm was injected into the downstream of $\text{N}_2 + \text{H}_2\text{O}$ plasmas discharged by 2.45 GHz microwave of 500 W and 6 inch silicon wafers covered by silicon dioxide as etching sample were placed in the downstream of the NF_3 injected point. The maximum etching rate was obtained in the treatment with 5% water vapor but no etching occurred in the treatment with higher water vapor mixing ratio than 25%.

15 In addition, native oxide removal was confirmed by the result that the hydrophilic surface of a 6 inch Si wafer covered by native oxide was turned to hydrophobic after 3 minutes of downstream treatment. Then microwave power was 500 W, pressure was 2.0 Torr, flow rate of NF_3 was 100 sccm, and flow rate of water vapor and nitrogen was 10 sccm and 190 sccm.

20

2. Second Example

Fig. 6 shows dependence of etching depth of SiO_2 on the mixing ratio of water vapor and nitrogen in the surface treatment using the equipment shown in Fig. 2, for example. In this treatment, NF_3 of 100 sccm was injected into the downstream region of $\text{N}_2 + \text{NH}_3$ plasmas discharged by 2.45 GHz microwave of 500 W and 6 inch silicon wafers covered by silicon dioxide as etching sample were placed in the downstream of the NF_3 injected point. Nitrogen gas containing lower concentration of NH_3 than a selected percentage based upon Fig. 6. served good etching result.

30 Additionally, native oxide removal was also confirmed by the result that the hydrophilic surface of a 6-inch silicon wafer covered by native oxide was turned to hydrophobic after 3-min downstream treatment. Then microwave power was 500 W, pressure was 4.0 Torr, and flow rates of NF_3 , NH_3 , and nitrogen are shown in Fig. 6.

3. Third Example

Silicon substrate placed on the treatment heat stage in the equipment shown in Fig. 2 is processed in downstream of a nitrogen plasma with 5% of water-vapor (10 sccm). Flow rate of nitrogen containing 5% of water vapor was total 200 sccm. Applied microwave (2.45 GHz) was 500 W to generate plasma. In this treatment, silane gas of 5 sccm was injected at the downstream. Substrate temperature was kept at 450 degree C during processing and treatment time was 1 hour under pressure at 2 Torr. By the processing, certain deposited film was formed on the silicon wafer surface and the surface of the film was hydrophilic.

After dipping this sample into 5% of HF diluted solution for 1 minute, the silicon surface became the hydrophobic. This indicates that the deposited material must be some kind of silicon-oxide-material.

4. Fourth Example

Silicon substrate placed on the treatment heat stage in the equipment shown in Fig. 2 is processed in downstream of a nitrogen plasma with 5% of water-vapor (10 sccm). Flow rate of nitrogen containing 5% of water vapor was total 200 sccm. Applied microwave (2.45GHz) was 500 W to generate plasma. In this treatment, ethyl alcohol of 5 sccm was injected at the downstream. Substrate temperature was kept at 600 degree C during processing and treatment time was 3 hr. By this treatment, silicon wafer surface was discolored by a deposited film. In order to probe what this deposited material was, the sample was treated with plasma ashing system.

Fig. 7 shows the barrel type plasma ashing system is used to process wafer 35 on the wafer carrier 34 by oxygen plasma which is generated inside of quartz reaction tube 31 induced oxygen and supplied RF power into the electrode 32a and 32b from RF generator 33. Wafer 35 is load and unload at the part of open side of quartz tube 31, and use cover 36 at the processing time to cover quartz open side. Aluminum etch tunnel 37 is also available. Previous processed Si wafer with a deposition film was processed with this type of oxygen ashing system under conditions of oxygen gas flow 500 sccm, 1 Torr and 300 watt RF power for 30 minutes. This processing stripped previously observed deposited material. This is the indication that previous deposit

material should be some type of carbon content material such as amorphous carbon or diamond like carbon. The result shows that this method can be used to produce carbon composite material film include diamond.

5 As above description, surface treatment in which atomic hydrogen was the one of the necessary species is realized by the use of a gas mixed a gas containing essentially water vapor and a gas containing nitrogen, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and/or radon (Rn), through the catalytic effect induced on nitrogen, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and/or radon (Rn) by the plasma, though water vapor was used for the source of atomic
10 hydrogen. Accordingly, this invention makes it possible to inexpensively and safely use the atomic hydrogen surface treatment without special safety protection system and circumstance.

For example, in comparison with conventional water vapor added hydrogen plasma system, this technology can substantially eliminate the load lock
15 module, object transfer system specialized to load lock environment, pumping package applicable to hydrogen evacuation, exhaust gas treatment system, safety and alert system, and other hardware. Thus, this invention provides the cost reduction of this system over 10,000,000 yen per unit (in 1998) depending on the purpose of system and the condition of operation.

20 While the above is a full description of the specific embodiments, various modifications, alternative constructions and equivalents may be used. Therefore, the above description and illustrations should not be taken as limiting the scope of the present invention which is defined by the appended claims.

WHAT IS CLAIMED IS:

1 1. A method of surface treatment of materials at a downstream
2 region of a plasma source, said method comprising steps of:
3 generating a plasma from a gas-C in a plasma source, said gas-C
4 comprising a gas-A and a gas-B, said gas-A selected from a compound comprising at
5 least a nitrogen bearing compound or an other gas, said other gas being selected from a
6 mixture of an element in group 18 classified in the atomic periodic table, said gas-B
7 comprising at least a NH₃ bearing compound;
8 injecting a gas-D downstream of said plasma source of said gas C;
9 setting an object downstream of the gas-D injection and downstream of
10 said plasma source, said object comprising a surface; and
11 processing said surface of said object by a mixture species generated
12 from said gas-C in said plasma and said gas-D;
13 wherein said NH₃ bearing compound in said gas-C includes a NH₃
14 bearing concentration that is lower than an explosion limit for NH₃ gas.

1 2. The method of claim 1 wherein said object is a semiconductor
2 wafer, said semiconductor wafer including a thin layer of oxide thereon, said NH₃ bearing
3 compound forming an entity that substantially maintains said thin layer of oxide on said
4 semiconductor wafer.

1 3. The method of claim 1 wherein said species comprises atomic
2 hydrogen.

1 4. The method of claim 1 wherein said process occurs in an apparatus
2 that is substantially free from a load lock module.

1 5. The method of claim 1 wherein said other gas comprises one
2 selected from helium, neon, argon, krypton, xenon, or radon.

1 6. The method of claim 1 wherein said nitrogen bearing compound is
2 selected from N₂ or NF₃.

1 7. The method of claim 1 wherein said plasma is maintained by a
2 microwave source.

- 1 8. The method of claim 1 wherein said plasma is provided in a
2 microwave cavity.
- 1 9. A method of surface treatment of materials at a downstream
2 region of a plasma source, said method comprising:
3 generating a plasma from a gas-A and a gas-B, said gas-A selected from
4 a compound comprising at least a nitrogen bearing compound and said gas-B comprising
5 at least a NH_3 bearing compound;
6 injecting a gas-D downstream of said plasma source of said gas A and
7 gas B;
8 setting an object downstream of the gas-D injection and downstream of
9 said plasma source, said object comprising a surface; and
10 processing said surface of said object by a mixture species generated
11 from said gas A and gas B in said plasma and said gas-D;
12 wherein said NH_3 bearing compound is lower than an explosion limit for
13 NH_3 gas.
- 1 10. The method of claim 9 wherein said gas D is selected from a silane,
2 an alcohol, and NF_3 .
- 1 11. The method of claim 9 wherein said species comprises atomic
2 hydrogen.
- 1 12. The method of claim 9 wherein said process occurs in an apparatus
2 that is substantially free from a load lock module.
- 1 13. The method of claim 9 wherein said nitrogen bearing compound is
2 selected from N_2 or NF_3 .
- 1 14. The method of claim 9 wherein said plasma is maintained by a
2 microwave source.
- 1 15. The method of claim 9 wherein said plasma is provided in a
2 microwave cavity.
- 1 16. Apparatus for processing an object, said apparatus comprising:

2 a chamber;
3 a plasma discharge room coupled to said chamber, said plasma discharge
4 room being downstream from said chamber;
5 a first gas supply comprising a gas A coupled to said plasma discharge
6 room, said gas A comprising a nitrogen bearing compound;
7 a second gas supply comprising a gas B coupled to said plasma discharge
8 room, said gas B comprising an NH_3 bearing compound;
9 a third gas supply comprising a gas D coupled between said plasma
10 discharge room and said chamber; and
11 a susceptor in said chamber for holding an object to be processed.

1 17. The apparatus of claim 16 wherein said gas D is selected from a
2 silane, an alcohol, and NF_3 .

1 18. The apparatus of claim 16 wherein said apparatus is substantially
2 free from a load lock module.

1 19. The apparatus of claim 16 wherein said nitrogen bearing compound
2 is selected from N_2 or NF_3 .

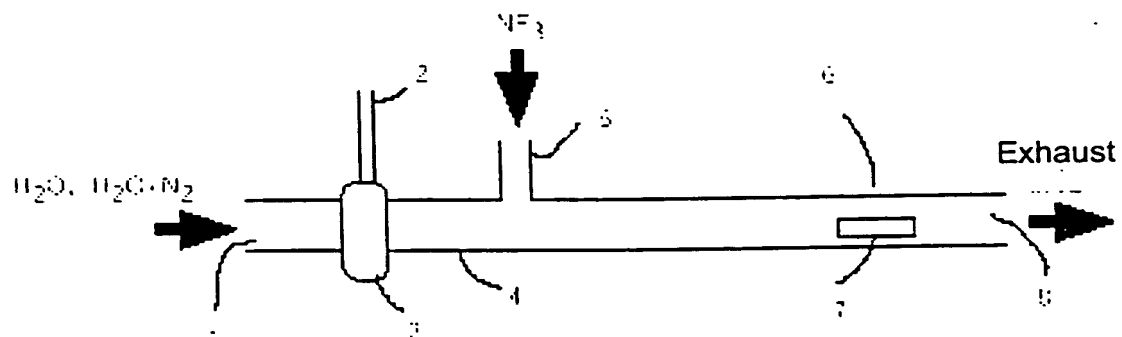
1 20. The apparatus of claim 16 wherein said plasma is maintained by a
2 microwave source.

PLASMA SURFACE TREATMENT METHOD AND RESULTING DEVICE

ABSTRACT OF THE DISCLOSURE

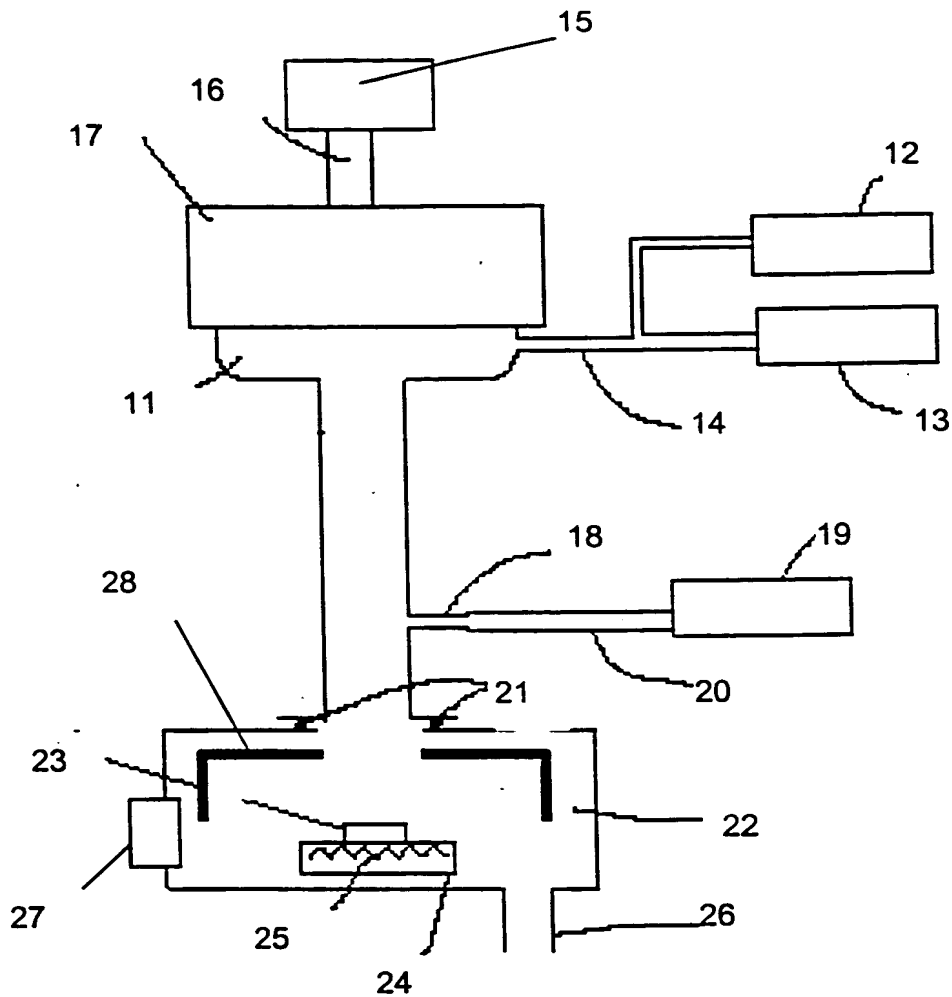
The present invention provides a method for treating a surface of an object using, for example, a downstream region of a plasma source. The method includes a step of generating a plasma from a gas-C in a plasma source, where the gas-C includes a gas-A and a gas-B. Gas-A is selected from a compound comprising at least a nitrogen bearing compound or an other gas. The other gas is selected from a mixture of an element in group 18 classified in the atomic periodic table. Gas-B includes at least a NH_3 bearing compound. The method also includes a step of injecting a gas-D downstream of the plasma source of the gas-C. The method also includes a step of setting an object (having a surface) downstream of the gas-D injection and downstream of the plasma source. A step of processing the surface of the object by a mixture species generated from the gas-C in the plasma and the gas-D is included. The NH_3 bearing compound in the gas-C includes a NH_3 bearing concentration that is lower than an explosion limit of NH_3 , which is safer than conventional techniques.

Fig.1



- 1 #1 Gas inlet
- 2 Micro wave guide
- 3 Microwave cavity
- 4 #2 Gas inlet
- 5 Chamber
- 6 Treatment room
- 7 Silicon substrate
- 8 Exhaust

Fig.2



- 11 Plasma discharge room
- 12 Gas-A supply unit
- 13 Gas-B supply unit
- 14 Fitting
- 15 Microwave generator
- 16 Wave guide
- 17 Microwave cavity
- 18 Nozzle
- 19 Gas-D supply unit
- 20 Fitting

- 21 O-ring
- 22 Treatment room
- 23 Treatment material
- 24 Treatment stage
- 25 SiC heater unit
- 26 Vacuum Exhaust port
- 27 Loading & Unloading port
- 28 Inside wall

Fig.3

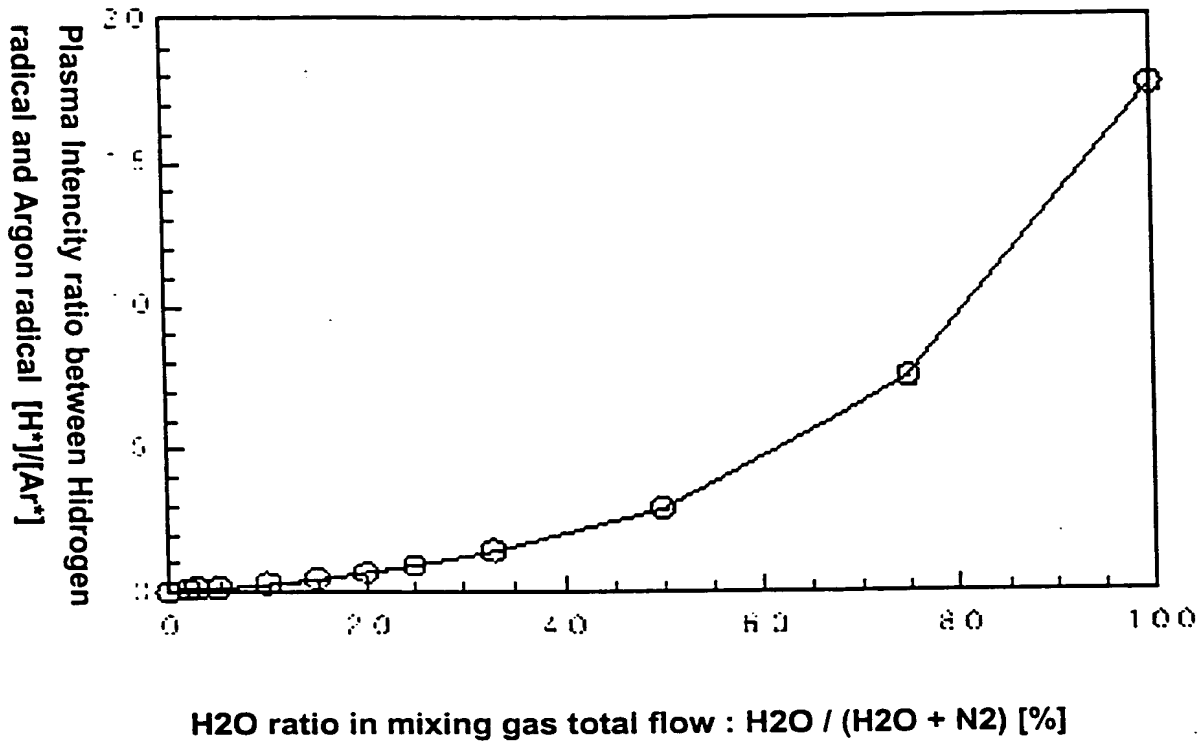
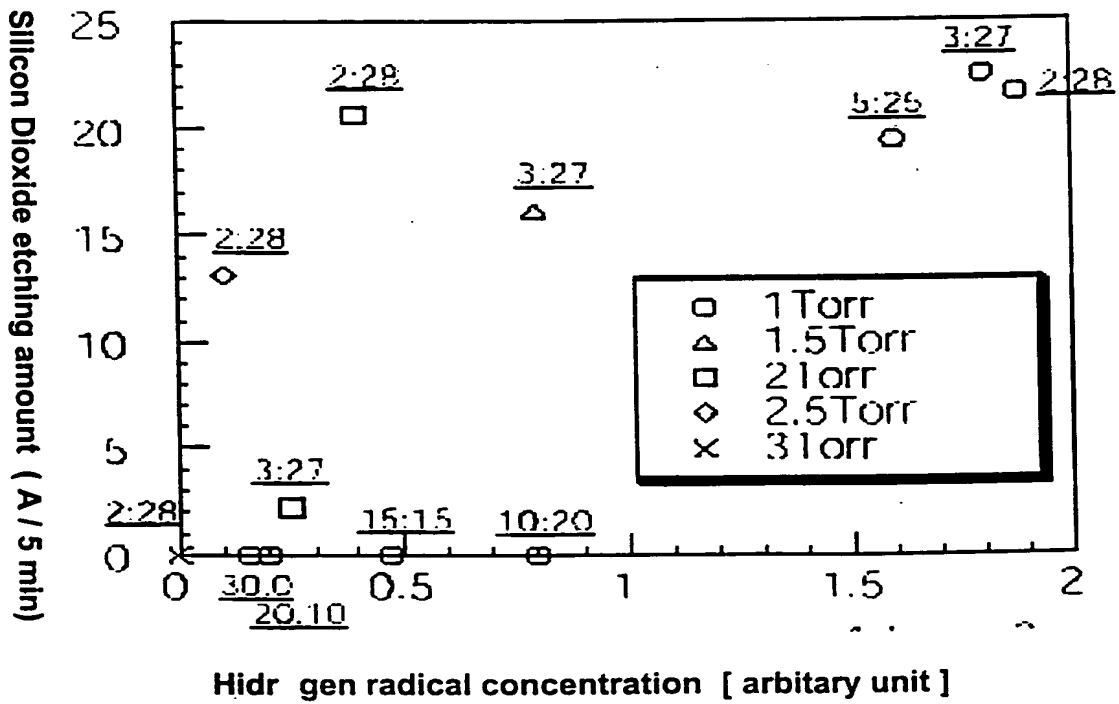


Fig.4



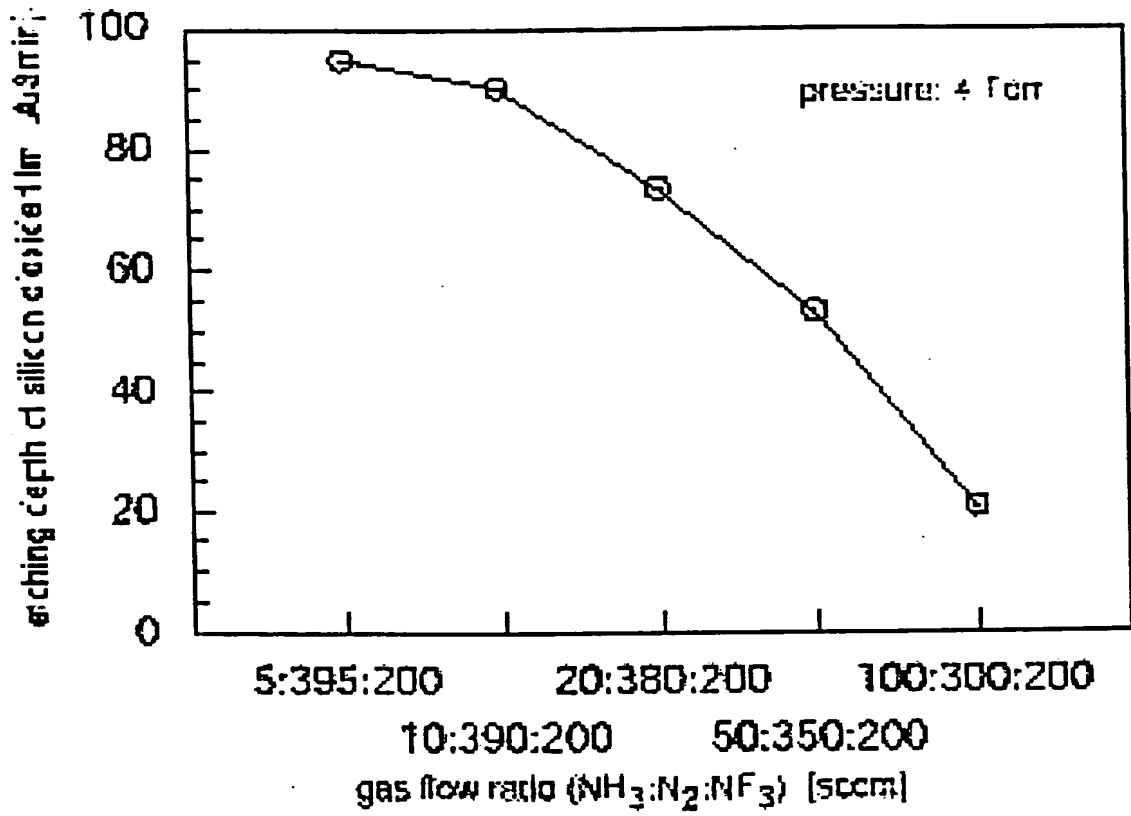


FIG. 6

Fig.5

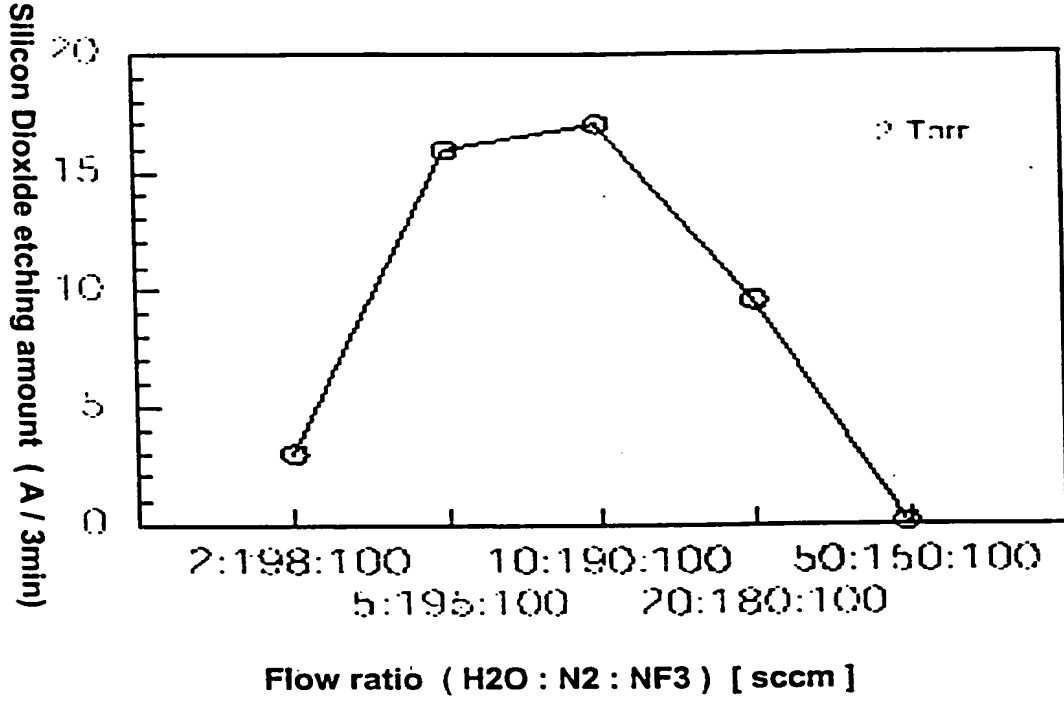
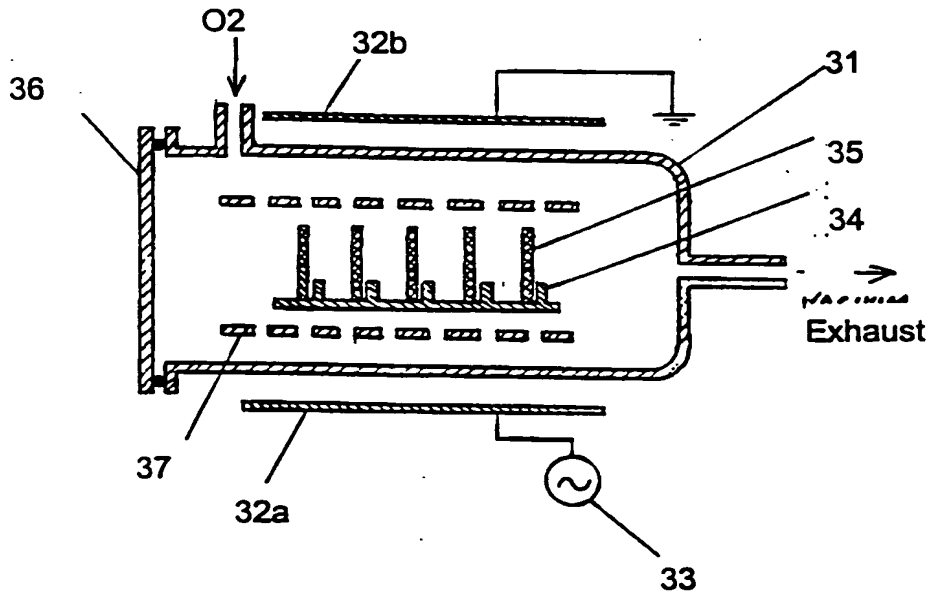


Fig.7



- 31 Quartz reaction tube
- 32a, 32b Electrode
- 33 RF generator
- 34 Wafer carrier
- 35 Wafer
- 36 Cover
- 37 Aluminum etch tunnel